

# Supporting Information

## Ultrasound-induced Organogel Formation Followed by Thin Film Fabrication via Simple Doctor Blading Technique for Field-Effect Transistor Applications

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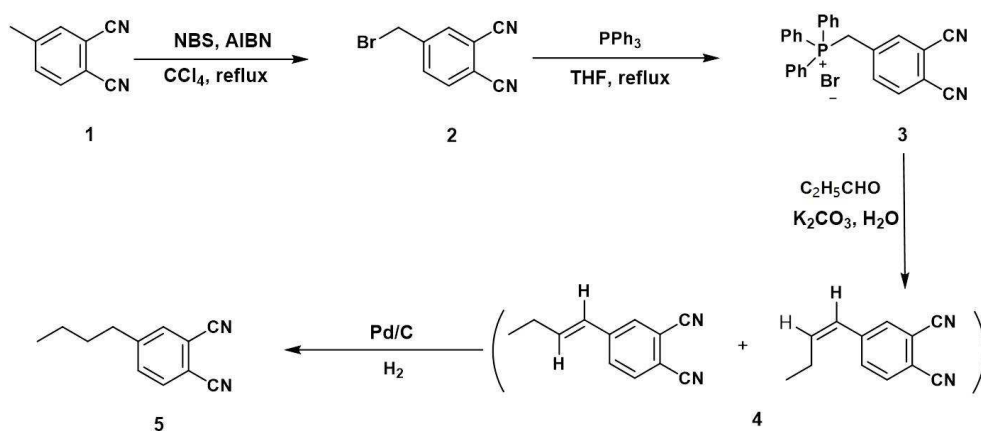
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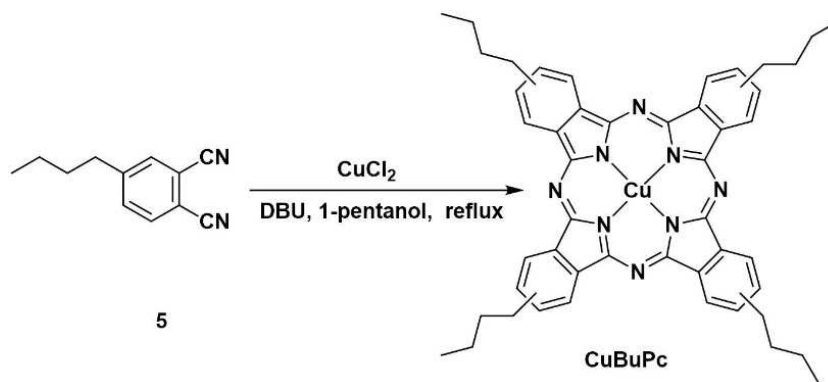
## General Experimental

### Materials Synthesis

All materials were purchased from Sigma-Aldrich and used as received.  $^1\text{H}$  NMR spectra were obtained from  $\text{CDCl}_3$  solutions on a Bruker Ascend 400 NMR spectrometer at 298 K. High-resolution mass spectrometry measurements were recorded on a Q-Exactive mass spectrometer. UV-vis spectra were recorded on ThermoScientific EVOLUTION 201 UV-vis spectrometer. The synthetic routes are illustrated in Scheme S1 and S2.



Scheme S1. Synthetic route to 4-butylphthalonitrile.



Scheme S2. Synthesis of unsymmetrical tetra-*n*-butyl-substituted copper(II) phthalocyanine.

### 4-Bromomethylphthalonitrile (2)

Carbon tetrachloride (1 L) was added to a mixture of 4-methylphthalonitrile (12 g, 82.2 mmol), N-bromosuccinimide (24 g, 134.8 mmol), and azobisisobutyronitrile (0.6 g, 3.65 mmol) in a two-neck round-bottom flask under an inert atmosphere of argon. The suspension was stirred at 80 °C for 12 h. The suspension was filtered, the residue washed with  $\text{CH}_2\text{Cl}_2$  (200 mL) and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ /petroleum ether (v/v, 1/1) as the eluent to afford **2** as a white solid (9.1 g, 50%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.85 (d,  $J = 1.8$  Hz, 1H, phenyl's H), 7.81 (d,  $J = 8.1$  Hz, 1H, phenyl's H), 7.76 (dd,  $J = 8.1, 1.8$  Hz, 1H, phenyl's H), 4.49 (s, 2H,  $-\text{CH}_2$ ).

### **(3,4-Dicyanobenzyl)triphenylphosphonium bromide (3)**

Tetrahydrofuran (600 mL) was added to a mixture of triphenylphosphine (5.4 g, 20.6 mmol) and 4-bromomethylphthalonitrile (**2**) (3.0 g, 13.7 mmol). The mixture was stirred at reflux for 24 h. The reaction mixture was allowed to cool to room temperature and petroleum ether was added (300 mL). The resulting suspension was stirred for 5 min at room temperature and then filtered. The precipitate was washed with CH<sub>2</sub>Cl<sub>2</sub>/petroleum (v/v, 1/2) and then dried under ambient conditions to give **3** as a white solid (6.6 g, 40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.07 (d, *J* = 8.2 Hz, 1H, phenyl's H), 7.87–7.79 (m, 9H, phenyl's H), 7.67–7.63 (m, 6H, phenyl's H), 7.55 (d, *J* = 8.2 Hz, 1H, phenyl's H), 7.48 (s, 1H, phenyl's H), 6.11 (d, *J* = 15.8 Hz, 2H, –CH<sub>2</sub>).

### **4-Butenylphthalonitrile (4)**

A solution of propanal (5 mL) and potassium carbonate (0.49 g, 3.6 mmol) in H<sub>2</sub>O (10 mL) was added to **3** (0.58 g, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred at room temperature for 2 h. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL × 3), and the combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (v/v, 1/1) as the eluent to give **4** (0.18 g, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.79–7.59 (m, 3H, phenyl's H), 6.55–5.90 (m, 2H, CH=CH), 2.50–2.28 (m, 2H, –CH<sub>2</sub>), 1.08–1.05 (m, 3H, –CH<sub>3</sub>).

### **4-Butylphthalonitrile (5)**<sup>1</sup>

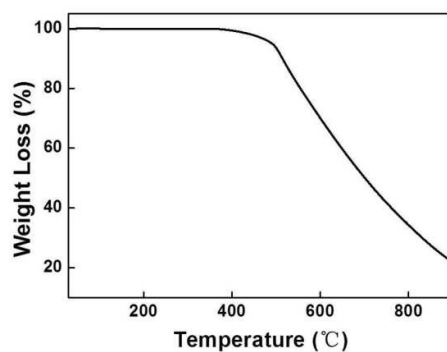
Olefin **4** (1.0 g, 5.4 mmol), palladium on carbon (10%, 0.50 g), and ethanol (30 mL) were added to a round-bottom flask. The suspension was stirred at room temperature under an atmosphere of hydrogen for 8 h. The resulting mixture was filtered, and the residue washed with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The filtrate was collected and the solvent removed by rotary evaporation. The crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (v/v, 1/1) as the eluent to give **5** (0.90 g, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 1H, phenyl's H), 7.62 (d, *J* = 1.6 Hz, 1H, phenyl's H), 7.54 (dd, *J* = 8.1, 1.8 Hz, 1H, phenyl's H), 2.73 (t, *J* = 7.6 Hz, 2H, –CH<sub>2</sub>), 1.69–1.59 (m, 2H, –CH<sub>2</sub>), 1.41–1.32 (m, 2H, –CH<sub>2</sub>), 0.95 (t, *J* = 7.3 Hz, 3H, –CH<sub>3</sub>).

### **Tetra-*n*-butyl-substituted copper(II) phthalocyanine (CuBuPc) (Scheme S2)**

A mixture of **5** (1.0 g, 5.4 mmol), copper(II) chloride (0.24 g, 1.8 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mL), and 1-pentanol (2 mL) were stirred at reflux under argon for 2 h. The reaction mixture was cooled to room temperature and petroleum ether (50 mL) added to precipitate the product. The suspension was stirred for 5 min, filtered and the residue washed with CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The filtrates were combined and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/ethanol (v/v, 1/3) as the eluent to give a blue product. The product was further purified by repeated recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ethanol to give CuBuPc (0.38 g, 35%). To fulfill the requirements of electronic applications, the product was further purified by vacuum sublimation in a sublimation machine (Technol VDS-80) operated at 400 °C and ~3 × 10<sup>-3</sup> Pa. Elemental analysis calcd (%) for C<sub>48</sub>H<sub>48</sub>CuN<sub>8</sub>: C, 72.02; H, 6.04; N, 14.00; found: C, 71.89; H, 6.10; N, 13.89. ESI-MS: *m/z* (M<sup>+</sup>) 799.33. UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 678 nm (195625 L·mol<sup>-1</sup>·cm<sup>-1</sup>), 611 nm (43360 L·mol<sup>-1</sup>·cm<sup>-1</sup>). IR (KBr): ν = 2950, 2924, 2855, 1611, 1504, 1456, 1405, 1337, 1159, 1095, 1064, 819, 737, 720 cm<sup>-1</sup>.

### Thermogravimetric analysis (TGA)

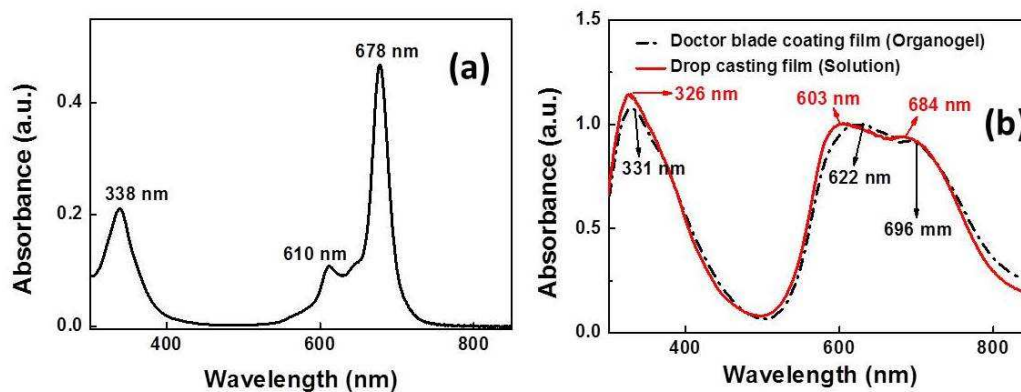
A few milligrams of solid sample were loaded on a platinum crucible. Weight loss of each sample was recorded with a Discovery TGA analyzer between 50 and 850 °C at rate of 10 °C/min under a flowing N<sub>2</sub> stream.



**Figure S1.** TGA curve of CuBuPc.

### UV-Vis absorption analysis

The UV-Vis spectra was performed on a Thermo scientific EVOLUTION 201 operated at a rate of 1 nm/step ranging from 200 to 1100 nm. The CuBuPc thin films were prepared on ITO glass via doctor-blading and drop-casting methods.



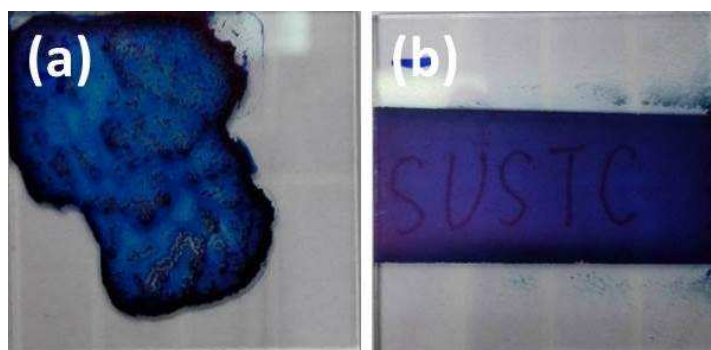
**Figure S2.** UV-Vis absorption spectra for (a) CuBuPc solution in 1,2-dichlorobenzene, and (b) CuBuPc thin films fabricated on ITO glass by doctor blading and drop-casting.

### Rheological measurement

The rheological behavior of CuBuPc organogel was measured according to a literature method using a Varion MICRO system.<sup>2</sup> A frequency sweep analysis was carried out with the CuBuPc gel, where the dynamic mechanical properties (*e.g.*, storage modulus  $G'$  and loss modulus  $G''$ ) were recorded as a function of angular frequency at a constant strain of 0.1% at 25 °C.

## Electron microscopy

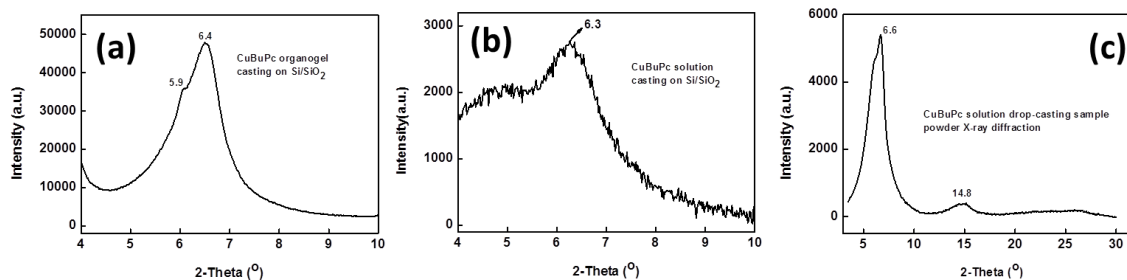
Morphologies of the organogel were recorded by atomic force microscopy (AFM) using a MFP-3D-Stand Alone scanning probe in tapping mode. Samples were prepared on a SiO<sub>2</sub>/Si substrates by doctor blading from CuBuPc organogel and drop casting from CuBuPc solution in 1,2-dichlorobenzene following the same manufacturing procedures for the fabrication of transistor devices. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) measurements were undertaken on a Tecnai F30 S-TWIN with an accelerating voltage of 200 kV. The samples were prepared by placing a drop of a dilute solution obtained from gel-phase material or CuBuPc solution on carbon-coated copper grids. The grid was then allowed to dry under ambient conditions.



**Figure S3.** Photographs of CuBuPc films formed on ITO glass by (a) drop casting from CuBuPc solution in 1,2-dichlorobenzene, and (b) Doctor blading from CuBuPc organogel.

## X-ray diffraction

Grazing incidence X-ray diffraction patterns of deposited films formed on SiO<sub>2</sub>/Si were recorded using a Smartlab 9 kW diffractometer with a Göbel mirror attachment. Irradiation of the parallel CuK $\alpha_{1,2}$  X-ray beam was fixed at a grazing incident angle of 1.000°( $\theta$ ) and the detector was independently moved to collect the diffraction data in 2 $\theta$  range of 4°–10° with a step-size of 0.02° (2 $\theta$ ) at a fixed speed of ca. 5 s/step. The X-Ray powder diffraction (XRPD) measurements were performed on the same diffractometer using a scanning rate of 0.02°/step at a fixed speed of ca. 5 s/step in the 2 $\theta$  range from 4° to 30°. The XRPD samples were prepared by dropping a freshly prepared organogel onto silicon wafer substrates and drying them under atmosphere at 50 °C.



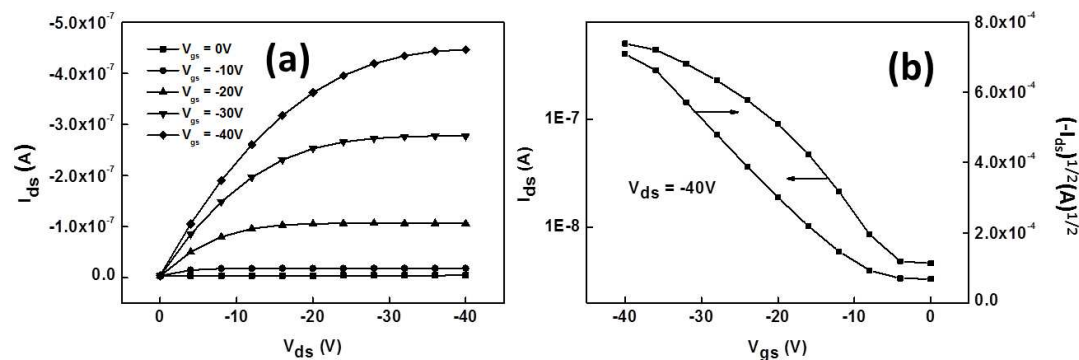
**Figure S4.** GIXRD patterns of CuBuPc films formed on Si/SiO<sub>2</sub> substrates by doctor blading from (a) CuBuPc organogel and (b) drop casting from CuBuPc solution in 1,2-dichlorobenzene, (c) XRPD pattern of drop-casting CuBuPc solution.

## Device fabrication and characterization

A heavily doped silicon substrate was used as the gate electrode. A silicon dioxide dielectric layer (100 nm) was thermally grown on the silicon substrate. Image reversal photolithography followed by standard lift-off process was used to form the Ti/Au source/drain contact patterns. The fabricated field-effect transistors had a channel width  $W$  around 1000–30000  $\mu\text{m}$  and a channel length  $L$  within 2–100  $\mu\text{m}$ . The bottom-contact field-effect transistors were fabricated on the patterned  $\text{SiO}_2/\text{Si}$  substrate by drop casting and doctor blade casting process. The output and transfer characteristics of the field-effect transistors were measured under ambient condition on a probe station connected to a semiconductor parameter analyzer (Keithley 4200 SCS). The field-effect charge mobility  $\mu$  was obtained from the output characteristics in the saturated regime according to the equation:

$$I_{ds} = \frac{W}{2L} \mu C_i (V_g - V_t)^2$$

Here,  $I_{ds}$  and  $V_{ds}$  are the current and voltage bias between the drain and the source of OFET respectively,  $V_g$  represents the gate voltage,  $L$  is the conducting channel length,  $W$  the conducting channel width,  $\mu$  the field-effect mobility,  $C_i$  the capacitance of the insulating  $\text{SiO}_2/\text{Si}$  layer, and  $V_t$  the threshold voltage.



**Figure S5.** (a) Output and (b) Transfer characteristics of bottom-contact (channel length 100  $\mu\text{m}$ , channel width 3000  $\mu\text{m}$ ) OFETs fabricated by drop casting from CuBuPc solution in 1,2-dichlorobenzene.

## References

- (1) Hanack, M.; Knecht, S.; Polcy, R.; Subramanian, L. R. Axially 1,4-Diisocyanobenzene Bridged Substituted Iron (II) Phthalocyanines and 2,3-Naphthalocyanines. *Synth. Met.* **1996**, *80*, 183–189.
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